U3-0113-TS (2)

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 203 351 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 86105424.5

(22) Date of filing: 18.04.86

(51) Int. Cl.⁴: G 01 N 27/56

(30) Priority: 19.04.85 JP 82388/85
30.08.85 JP 189752/85

(43) Date of publication of application: 03.12.86
Bulletin 86/49

(84) Designated Contracting States: DE FR GB

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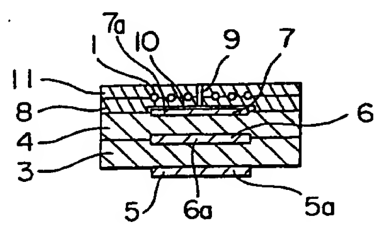
(54) Oxygen sensor element and process for producing the same.

(57) A solid electrolyte type oxygen sensor element having a built-in heater characterized by having an insulating layer including a heater therein on an electrode formed side of solid electrolyte plate is improved in adhesiveness when an oxide binder of $Al_2O_3 - SiO_2 - MgO$ system, or $Al_2O_3 - SiO_2$ system is added to the insulating layer, the solid electrolyte plates or an insulating thin layer formed at an interface of the insulating layer and the solid electrolyte plate. When an intermediate layer is interposed between the insulating layer and the solid electrolyte plate, cracks caused by thermal stress can be prevented effectively.



EP 0 203 351 A1

8602033 3/21.5

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April 18, 1986
A 6975-EP

OXYGEN SENSOR ELEMENT AND PROCESS FOR PRODUCING THE SAME

1 BACKGROUND OF THE INVENTION

This invention relates to an oxygen sensor element, particularly an oxygen sensor element having a built-in heater, and a process for producing the same.

Oxygen sensor elements practically used are constructed so as to expose one of porous electrodes sandwiching solid electrolyte plates to a gas to be measured (a partial pressure of oxygen being Pg) and to expose another porous electrode to a standard gas (a partial pressure of oyxgen being Pr), and detect a signal voltage Vs which is represented by the Nernst's equation as follows:

$$Vs \propto \ell n \frac{Pg}{Pr}$$

so as to measure an oxygen concentration in the gas to be measured.

In order to take out the signal voltage Vs, oxygen ions should flow through the solid electrolyte plates. When solid electrolyte plates made of ZrO_2 partially stabilized with Y_2O_3 are used, the signal voltage mentioned above cannot be obtained until the temperature of the oxygen sensor element becomes about 500°C or higher.

For example, the combustion control of cars is conducted by measuring the oxygen concentration in an exhaust gas which is a gas to be measured, and adjusting the ratio of air to fuel so as to carry out ideal combustion. In order to reduce a fuel cost of cars remarkably, it is necessary to operate such a controlling system from the start of the engine. Therefore, it is necessary to heat the oxygen sensor element with a heater until the temperature of the oxygen sensor element becomes 500°C or higher by heating with the exhaust gas. Further, in order to control with high precision, it is necessary to maintain the oxygen sensor element at a constant temperature by heating with the heater even after heating with the exhaust gas.

Problems of conventional oxygen sensor elements are explained referring to Figs. 10 and 11.

Fig. 10 is a schematic cross-sectional view showing an indirectly heating and solid electrolyte type oxygen sensor of prior art. Fig. 11 is a schematic cross-sectional view along the line XI-XI of Fig. 10. Such a solid electrolyte type oxygen sensor is disclosed in, for example, Japanese Patent Unexamined Publication Nos. 72286/77 and 130649/81.

In Fig. 10, numeral 2 denotes an oxygen sensor element having porous electrodes at the bottom portion of a solid electrolyte type oxygen sensor, and numeral 1 denotes a heater winding around the bottom portion of the oxygen sensor element 2 with a nichrome wire,

platinum wire, or the like. The heater 1 is connected to electric wires 1a and 1b for supplying electric power. Numeral 15 denotes a holder for the oxygen sensor element, and numeral 16 denotes a fixing means for holding the oxygen sensor element 2 and attached to the holder 15. The oxygen sensor element 2 comprises a first solid electrolyte plate 3 and a second solid electrolyte plate 4 (made of, for example, ZrO_2 partially stabilized by 6 mole % of Y_2O_3) and porous electrodes 5, 6 and 7 (formed by, for example, screen printing a platinum paste) formed on the solid electrolyte plates as shown in Fig. 11. To the porous electrodes 5, 6 and 7, signal voltage lead-out wires 5a, 6a and 7a (not shown in the drawing) are connected.

In the solid electrolyte type oxygen sensor thus constructed, the porous electrode 7 is exposed to a gas to be measured, and the oxygen in pores of the porous electrode 6 is taken as a standard gas (the amount of oxygen corresponding to the oxygen flowed from the porous electrode 6 to the porous electrode 7 being supplied from the porous electrode 5 to the porous electrode 6). The signal voltage represented by the Nernst's equation as mentioned above is detected and taken out by the signal voltage lead-out wires 5a, 6a, 7a to measure the oxygen concentration in the gas to be measured.

Since the prior art solid electrolyte type oxygen sensor is an indirectly heating type wherein the

oxygen sensor element 2 is heated from the outside by the heater 1 wound therearound in a coil state, there is a problem in that the heating rate is slow. Further since the heat is not conducted effectively to the oxygen sensor element 2, there is also a problem in that the consumed electric power of the heater 1 is large. In addition, there is a further problem to be improved in that since the distance between the heater 1 and the oxygen sensor element 2 is large, the temperature of the oxygen sensor element 2 changes even if constant electric power is supplied to the heater 1, which results in making it impossible to control the temperature of the oxygen sensor element 2 highly precisely and thus producing errors in measured oxygen concentration values.

On the other hand, in order to form a heater in adhesion to the oxygen sensor element, it is necessary to insulate the heater with a material excellent in insulating properties at high temperatures. But since such a material hardly reacts with the solid electrolyte plate, contact of the heater with the oxygen sensor element is very difficult.

SUMMARY OF THE INVENTION

It is an object of this invention to provide an oxygen sensor element overcoming the problems of the prior art, being low in consuming electric power of heater for heating an oxygen sensor element and excellent

in temperature control of the oxygen sensor element. It is another object of this invention to provide a process for producing such an oxygen sensor element.

This invention provides a solid electrolyte type oxygen sensor element having a built-in heater comprising porous electrodes and solid electrolyte plates containing ZrO_2 as a major component placed alternately, and an insulating layer formed on an electrode formed side of one of the solid electrolyte plates so as to have a gas introducing hole and a gas chamber which is formed over the electrode, said insulating layer including therein a heater and containing Al_2O_3 as a major component, an oxide binder solid soluble in both the solid electrolyte and the insulating layer being added either to one of the solid electrolyte plate and the insulating layer, or to an insulating thin layer containing Al_2O_3 as a major component and formed at an interface of the solid electrolyte plate and the insulating layer.

The oxygen sensor element having a built-in heater may further contain an intermediate layer which is made of a metal oxide mixture and has a thermal expansion coefficient between that of the solid electrolyte plate and that of the insulating layer, between the insulating layer and the solid electrolyte plate having the gas chamber formed electrode thereon, said intermediate layer having a gas introducing hole connected to the gas introducing hole in the insulating plate and

to the gas chamber.

This invention also provides a process for producing an oxygen sensor element having a built-in heater which comprises constructing a green sheet laminate by forming electrodes on green sheets of solid electrolyte plates containing ZrO_2 as a major component,

placing a green sheet of insulating layer including a heater, containing Al_2O_3 as a major component and having a gas introducing hole on an electrode formed side of the solid electrolyte plate so as to form a gas chamber over the electrode,

forming an insulating thin layer containing Al_2O_3 as a major component and an oxide binder solid soluble in both the solid electrolyte and the insulating layer at an interface of the insulating layer and the solid electrolyte plate provided that the oxide binder is not previously added to either the solid electrolyte plate or the insulating layer,

pressing the green solid electrolyte plates and the green insulating layer and the insulating thin layer if contained, and

sintering the resulting pressed product.

In the above-mentioned process, a green sheet of intermediate layer containing a metal oxide mixture having a linear thermal expansion coefficient between that of the solid electrolyte plate and that of the insulating layer can be placed between the green insulating layer and the green solid electrolyte plate before pressing.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic cross-sectional view of one example of oxygen sensor element having a built-in heater according to this invention.

Fig. 2 is a schematic cross-sectional view of essential portions of Fig. 1.

Fig. 3 is a flow chart showing a process for producing an oxygen sensor element according to this invention.

Fig. 4 is a graph showing heating properties of an oxygen sensor element according to this invention.

Fig. 5 is a schematic cross-sectional view of one example of oxygen sensor element having a built-in heater according to this invention.

Fig. 6 is a graph showing heating properties of an oxygen sensor element according to this invention.

Fig. 7 is a graph showing a relationship between the thermal expansion coefficient and the Al_2O_3 adding amount in the intermediate layer shown in Fig. 5.

Fig. 8 is a flow chart showing a process for producing an oxygen sensor element according to this invention.

Fig. 9 is a triangular diagram of the oxide binder system of Al_2O_3 - SiO_2 - MgO.

Fig. 10 is a schematic cross-sectional view of an indirectly heating type oxygen sensor of prior art.

Fig. 11 is a cross-sectional view along the

line XI-XI of Fig. 10.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention is based on an idea that effective heating of an oxygen sensor element can be attained by adhering a heater for heating the element directly to the element or by a built-in heater.

Oxygen sensor elements formed by a ceramic green sheet method have a structure, for example as shown in Fig. 11, comprising solid electrolyte plates 3 and 4 having oxygen ion conductivity and porous electrodes 5, 6 and 7 formed on the solid electrolytes. The operational function of the element can be obtained by comparing the oxygen amount in the pores in the porous electrode 6 taken as a standard oxygen chamber and the oxygen amount in a gas to be measured at the electrode 7. In such a case, the oxygen consumed between the electrodes 6 and 7, that is, the oxygen amount corresponding to the oxygen flowed from the electrode 6 to the electrode 7, is supplemented by flowing oxygen from the electrode 5 to the electrode 6. In order to heat the oxygen sensor element directly, a heater for heating the element directly is provided on an insulating layer 8 which is laminated on one side of the solid electrolyte plate 4 having the electrode 7 thereon as shown in Fig. 2. In Fig. 2, numeral 9 denotes a gas introducing hole and numeral 10 denotes a gas chamber for a gas to be measured.

The insulating layer 8 having a built-in heater 1 should have excellent adhesiveness to the oxygen sensor element after sintering. Al_2O_3 is in general a material having excellent insulating properties at high temperatures. But, it hardly reacts with ZrO_2 constituting the solid electrolyte mainly and is not solid soluble with ZrO_2. In order to solve such a problem, a material which reacts with both ZrO_2 and Al_2O_3 is used at an interface of the solid electrolyte plate 4 and the insulating layer 8. Alternatively, such a material is added to either the solid electrolyte plates 3, 4 or the insulating layer 8. For simplicity of the procedure, such a material is added to both solid electrolyte plates 3 and 4. Further, such a material preferably forms a liquid phase at the time of sintering in order to complete the sintering reaction in a short time.

Examples of such a material are preferably oxide binders of Al_2O_3 - SiO_2 - MgO system and Al_2O_3- SiO_2 system. Among the Al_2O_3 - SiO_2 - MgO system oxide binders, those fallen in the region encircled by curves A - B - C - D - E - A in the triangular diagram of Fig. 9 and having a melting point of 1500°C or lower are more preferable. In Fig. 9, individual points A, B, C, D and E have the following values in percents by weight:

	Al_2O_3	SiO_2	MgO
A	14.5	82.0	3.5
B	5.0	65.0	30.0
C	8.3	58.7	33.0
D	22.7	46.5	30.8
E	37.6	45.6	16.8

Among the Al_2O_3 - SiO_2 system oxide binders, those containing Al_2O_3 in an amount of 5 to 30% by weight and SiO_2 in an amount of 70 to 95% by weight are more preferable.

The solid electrolyte type oxygen sensor element having a built-in heater and applying oxygen ion conductivity having a structure, for example, as shown in Fig. 1 can be produced as follows.

A green oxygen sensor element is prepared by forming electrodes 5, 6 and 7 on green sheets of solid electrode plates 3 and 4 containing ZrO_2 as a major component. A green sheet of an insulating layer 8 provided a heater 1 thereon and made of an insulator containing Al_2O_3 as a major component is placed on the solid electrolyte plate 4 having the electrode 7 thereon so as to form a gas chamber 10 to which a gas to be measured such as an exhaust gas is introduced through a gas introducing hole 9. On the other hand, an oxide binder such as an Al_2O_3 - SiO_2 - MgO system oxide binder or an Al_2O_3 - SiO_2 system oxide binder which is solid soluble both in the solid electrolyte containing ZrO_2 as

a major component and the insulating layer containing Al_2O_3 as a major component, is added to either the solid electrolyte plates 3 and 4 or the insulating layer 8. Alternatively, an insulating thin layer containing Al_2O_3 as a major component and the oxide binder as a minor component is formed at an interface of the solid electrolyte plate 4 and the insulating layer 8. Then, the laminated green sheets of the solid electrolyte plates 3 and 4 and the insulating layer 8 are pressed, followed by sintering.

More concretely, a process for producing the oxygen sensor element having a built-in heater as shown in Fig. 1 can be carried out as shown in Fig. 3.

First, a ZrO_2 powder partially stabilized with Y_2O_3 is mixed with a conventional organic binder such as polyvinyl butyral, a conventional plasticizer such as butyl phthalate, butyl glycolate, and a conventional organic solvent such as trichloroethane, tetrachloroethylene, n-butanol, etc., to give a slurry, which is formed into a ceramic plate (a green sheet of 0.25 mm thick) by slip casting according to a doctor blade method. Then, the green sheet is cut to give solid electrolyte plates 3 and 4 having predetermined size and shape, e.g. 13 mm wide and 40 mm long. Using a platimum paste obtained by making a platinum powder a paste state with an organic material such as ethylcellulose and n-butyl carbitol acetate (diethylene glycol monobutyl ether acetate), a first electrode 5 and a second electrode 6

are formed on the solid electrode plate 3 by a screen printing method. In the same manner, a third electrode 7 is formed on the solid electrode plate 4. Further, in order to form a gas chamber 10 on the electrode 7 after sintering, an organic layer 12 made from e.g. ethylcellulose, polyvinyl butyral, is formed as shown in Fig. 3. As the insulating layer 8, a green sheet of 0.15 mm thick is formed in the same manner as mentioned above from a mixture of 90 parts by weight of Al_2O_3 and 10 parts by weight of oxide binder containing 30% by weight of Al_2O_3, 53% by weight of SiO_2 and 17% by weight of MgO. The green sheet of insulator is cut with the same size and shape as the solid electrolyte plates mentioned above and drilled a gas introducing hole 9 for a gas to be measured such as exhaust gas. Then, a heater is formed by screen printing the same platinum plaste as mentioned above on the insulating layer 8. In order to protect the platinum heater, an insulating layer 11 having a gas introducing hole 9 is placed on the insulating layer 8. The green solid electrolyte plates 3 and 4 and the insulating layers 8 and 11 are laminated and hot pressed at 90°C under a pressure of 30 kgf/cm^2. followed by sintering at 1500°C for 2 hours in the air. After sintering, a reaction phase is admitted near the interface of ZrO_2 of the solid electrolyte plate 4 and Al_2O_3 of the insulating layer 8 to give strong bonding.

Fig. 4 shows the results of heating test of

the oxygen sensor element using the heater mentioned above. As is clear from Fig. 4, an electric power necessary to heat the element to 800°C is about 7 W, which value is 1/10 or less of the value of 100 W in the case of the prior art indirectly heating type oxygen sensor.

In the above-mentioned embodiment, an oxide binder of Al_2O_3 - SiO_2 - MgO system having the composition within the region encircled by the curves A - B - C - D - E - A in the triangular diagram of Fig. 9 is used in order to melt at a temperature lower than the sintering temperature of the element (1500°C), to accelerate the sintering of Al_2O_3 and to match the sintering shrinkage with ZrO_2. It is also possible to match the sintering shrinkage by adjusting the particle distribution of ZrO_2 and Al_2O_3.

It is possible to use as the oxide binder a compound containing 5 to 30% by weight of Al_2O_3 and 70 to 95% by weight of SiO_2.

The oxide binder is mixed in an amount of preferably 5 to 15% by weight in the insulating layer, the remainder being alumina. If the amount of the oxide binder is more than 15% by weight, the amount of liquid phase generated at the time of sintering becomes too much to react undesirably with a sintering table placed in a sintering furnace, whereas if the amount is less than 5% by weight, the reaction phase with ZrO_2 cannot be obtained sufficiently to fail to obtain strong bonding.

As mentioned above, Al_2O_3 is an excellent material for producing the insulating layer 8 due to high insulating properties at high temperatures. But, the linear thermal expansion coefficient of Al_2O_3 is greatly different from that of ZrO_2. Therefore, when the insulating layer containing Al_2O_3 as a major component is directly adhered to the solid electrolyte plate containing ZrO_2 as a major component for lamination, there is a fear of destroying the oxygen sensor element due to a stress caused by the difference in thermal expansion coefficients of Al_2O_3 and ZrO_2 at the time of sintering or during the use at high temperatures. Further, since ZrO_2 and Al_2O_3 hardly react each other, it is difficult to make them into one body by sintering.

In order to solve such a problem, an intermediate layer having a value, preferably a middle value of linear thermal expansion coefficient between that of the solid electrolyte plate containing ZrO_2 as a major component and that of the insulating layer containing Al_2O_3 as a major component, and having reactivity with both of Al_2O_3 and ZrO_2 at the time of sintering, is interposed between the insulating layer and the solid electrolyte plate. As the intermediate layer, one made of ZrO_2 partially stabilized with 6 mole % of Y_2O_3 and containing 3% by weight of Al_2O_3 is preferable.

A solid electrolyte type oxygen sensor element having a built-in heater containing the intermediate layer therein has a structure as shown below.

That is, the oxygen sensor element comprises a first and second solid electrolyte plates laminated and containing partially stabilized ZrO_2 as a major component, porous electrodes individually connected to lead-out wires for taking out signal voltages formed on one of the joined surfaces of the solid electrolyte plates and two opposite surfaces of the joined surfaces of the solid electrolyte plates, an intermediate layer made of a metal oxide mixture having a linear thermal expansion coefficient value, preferably a middle value, between that of the solid electrolyte plate and that of an insulating layer formed on one of the solid electrolyte plates so as to have a gas chamber for a gas to be measured over the electrode on the solid electrolyte plate and a gas introducing hole connected to the gas chamber, and an insulating layer containing Al_2O_3 as a major component and having a heater built in and a gas introducing hole connected to the gas introducing hole of the intermediate layer.

Such an oxygen sensor element can be operated by heating the solid electrolyte plates with the heater, passing a gas to be measured to the gas chamber through the gas introducing hole, and taking out signal voltages with regard to the oxygen concentration of the gas to be measured from the lead-out wires.

The oxygen sensor element including the intermediate layer can be produced as follows.

There are used a green sheet of the first solid

electrolyte plate containing partially stabilized ZrO_2 as a major component and having two porous electrodes connected to lead-out wires for taking out the signal voltages on both surfaces thereof, a green sheet of the second solid electrolyte plate containing partially stabilized ZrO_2 as a major component and having a porous electrode connected to a lead-out wire for taking out the signal voltage on one surface thereof, a pair of green sheets of the insulating layer containing Al_2O_3 as a major component, and having a gas introducing hole and a heater which is placed on one surface of joint surfaces of the green sheets, and a green sheet of the intermediate layer containing a metal oxide mixture which reacts with the solid electrolyte plate and the insulating layer at the time of sintering and has a value, preferably a middle value, of linear thermal expansion coefficient after sintering between that of the solid electrolyte plate and that of the insulating layer, and having a gas introducing hole.

The two green sheets of solid electrolyte plates are laminated so as to place the porous electrodes and the green sheets alternately, the green sheet of intermediate layer is laminated on one surface of the solid electrolyte plates so as to form a gas chamber (using an organic material which is removed by sintering) over the electrode and to connect to the gas introducing hole, and the green sheets of insulating layer are

laminated on the intermediate layer so as to connect the gas introducing holes each other, followed by pressing and sintering in the same manner as explained previously.

More concretely, the oxygen sensor element having the intermediate layer as shown in Fig. 5 can be produced as follows.

The oxygen sensor element 2A can be formed by laminating a first solid electrolyte plate 3 and a second solid electrolyte plate 4, each containing ZrO_2 partially stabilized with 6 mole % by Y_2O_3, having a porous electrode 6 connected to a lead-out wire 6a at the joint surfaces of the solid electrolyte plates 3 and 4 and two porous electrodes 5 and 7 connected to lead-out wires 5a and 7a at opposite surfaces to the joint surfaces, these lead-out wires being used for taking out signal voltages, these electrodes being formed by using a platinum paste by a screen printing method, by laminating insulating layers 8a and 8b [made of a mixture containing 90 parts by weight of Al_2O_3 and 10 parts by weights of Al_2O_3 (30 wt%) - SiO_2 (53 wt%) - MgO (17 wt%)] having gas introducing holes 9a and 9b connected each other to a gas chamber 10 and a heater 1A (formed by using the platinum paste by a screen printing method) via an intermediate layer 12 (made of ZrO_2 partially stabilized with 6 mole % of Y_2O_3 and containing 3% by weight of Al_2O_3) which is placed so as to form the gas chamber 10 over the electrode 7, and, if necessary, by forming

a protective layer 14 (made of, for example, magnesium spinel) on the porous electrode 5.

The linear thermal expansion coefficient of the intermediate layer is 8.4 x 10^{-6}/°C in the temperature range of 20° to 800°C, said value being in the middle of the value of the first and second solid electrolyte plates 3 and 4 (8.8 x 10^{-6}/°C in the above-mentioned temperature range) and the value of the insulating layers 8a and 8b (8.0 x 10^{-6}/°C in the above-mentioned temperature range). Since the stress due to the difference in the thermal expansion is relaxed by interposing the intermediate layer 12 between the solid electrolyte plate 4 and the insulating layer 8b, the oxygen sensor element 2A is not destroyed at the time of sintering (mentioned below) or during the use wherein the oxygen sensor element 2A is heated to about 800°C by the heater 1A. Further since the intermediate layer 12 reacts with the both the solid electrolyte plate 4 and the insulating layer 8b, the adhesiveness of the intermediate layer 12 to the solid electrolyte plate 4 and the insulating layer 8b is good, which results in easily sintering individual green sheets into one body to give the oxygen sensor element 2A with excellent mechanical strength.

When the thus produced solid electrolyte type oxygen sensor element 2A is exposed to a gas to be measured and switched on, an electric current is passed through the heater 1A until the temperature of the gas

to be measured is raised to the predetermined value of 800°C. Since the oxygen sensor element 2A can effectively be heated by the heater 1A, the oxygen concentration of the gas flowed to the gas chamber 10 from the gas introducing hole 9a can be measured easily with high precision irrespective of the temperature of the gas to be measured.

Effects of the oxygen sensor element 2A are explained referring to Fig. 6, which is a graph showing the heater heating properties of the solid electrolyte type oxygen sensor element shown in Fig. 5.

As is clear from Fig. 6, the consumed electric power necessary for heating the oxygen sensor element 2A to 800°C is about 10 W, which value is about 1/10 of the value of about 100 W in the case of the prior art indirectly heating type oxygen sensor shown in Fig. 10.

Further, since there is no gap between the heater 1A and the oxygen sensor element 2A and made into one body, the precision for temperature control of the oxygen sensor element 2A is improved to ±5°C from ±20°C. Therefore the precision of the oxygen concentration measurement is improved in about 4 times. Further, when the solid electrolyte type oxygen sensor element of this embodiment is used for combustion control of car engines, high precision control of combustion can be carried out from the start of the engine. Therefore, the fuel cost can be reduced in

about 10% compared with the use of prior art indirectly heating type oxygen sensor.

In the above-mentioned embodiment, ZrO_2 partially stabilized with 6 mole % Y_2O_3 is used as the solid electrolyte plates 3 and 4 in the oxygen sensor element 2A, but the material for the solid electrolyte plates is not limited to such a composition. For example, there can be used ZrO_2 partially stabilized with 4 to 8 mole % of Y_2O_3 or 4 to 8 mole % of CaO.

Further, the material for the insulating layers 8a and 8b is not limited to the composition comprising 90 parts by weight of Al_2O_3 and 10 parts by weight of an oxide binder of Al_2O_3 (30 wt. %) - SiO_2 (53 wt. %) - MgO (17 wt. %). As the oxide binder, it is preferable to use oxides having the composition encircled by the curve A - B - C - D - E - A in the triangular diagram of Fig. 9 and oxides of Al_2O_3- SiO_2 system wherein Al_2O_3 is 5 to 30% by weight and SiO_2 is 70 to 95% by weight. It is also possible to use Al_2O_3 - SiO_2 - CaO system oxides. Further, Al_2O_3 single body can also be used, when the particle size is reduced. The sintering temperature of it is close to that of the solid electrolyte, and the sintering shrinkage is matched to that of the solid electrolyte plate.

The material for the intermediate layer 12 is not limited to ZrO_2 partially stabilized with 6 mole % Y_2O_3 and containing 3% by weight of Al_2O_3. The amount of Al_2O_3 to be added is limited as explained bellow referring

to Fig. 7.

Fig. 7 is a graph showing a relationship between the thermal expansion coefficient and the adding amount of Al_2O_3 to the intermediate layer shown in Fig. 5. As is clear from Fig. 7, when the Al_2O_3 adding amount is less than 1.5% by weight, the linear thermal expansion coefficient becomes large and close to that of the solid electrolyte plate 4, which results in making the adhesiveness of the intermediate layer to the insulating layer 8b worse. On the other hand, when the Al_2O_3 adding amount is more than 4% by weight, the linear thermal expansion coefficient becomes small and close to that of the insulating layer 8b, which results in reducing the thermal stress relaxation effect even if the intermediate layer is interposed. Therefore, preferable adding amount of Al_2O_3 is 1.5 to 4% by weight.

Further, as the material for the intermediate layer, there can be used any metal oxides which react with the solid electrolyte plate 4 and the insulating layer 8b at the time of sintering, and have a linear thermal expansion coefficient value after sintering between that of the solid electrolyte plate and that of the insulating layer. For example, there can be used metal oxides of Al_2O_3 - SiO_2 system, metal oxides of Al_2O_3 - TiO_2 system.

In the above embodiment, the protective layer 14 is formed on the porous electrode 5, but the use of the protective layer is not essential. But the use of

a the protective layer is advantageous in that adhesion of dusts and peeling of the porous electrode 5 due to collisions of exhaust gas can be prevented, and thus the life of the porous electrode 5, in other words the life of the oxygen sensor element 2A can be prolonged.

One embodiment of the process for producing the solid electrolyte type oxygen sensor element 2A of Fig. 5 is explained below referring to Fig. 8.

Fig. 8 is a flow chart showing one embodiment of the process for producing an oxygen sensor element in a solid electrolyte type oxygen sensor according to this invention. In Fig. 8, the same reference numbers as used in Fig. 5 are used.

A ZrO_2 powder partially stabilized with 6 mole % Y_2O_3 is mixed with a conventional organic binder, a conventional plasticizer, a conventional organic solvent to give a slurry, which is formed into a plate-like green sheet (0.25 mm thick) by slip casting according to a doctor blade method. Then, the green sheet is cut to give a first solid electrolyte plate 3 having predetermined size. On both sides of the solid electrolyte plate 3, porous electrodes 5 and 6 connected to lead-out wires 5a and 6a for taking out signal voltages are formed by screen printing a platinum paste obtained by mixing a platinum powder with an organic material. A second solid electrolyte plate 4 is cut from the green sheet in the same manner with the same size as in the case of the first solid electrolyte plate 3. A porous

electrode 7 connected to a lead-out wire 7a for taking out a signal voltage is formed on one surface of the solid electrolyte plate 4 in the same manner as in the case of forming the electrodes 5 and 6. On the porous electrode 7, an organic material 13 (which can burn at about 300°C and below the sintering temperature, e.g. ethylcellulose, polyvinyl butyral, etc.) as a core for forming a gas chamber 10 is formed by a screen printing method (or alternatively, a film-like material may be adhered).

A green sheet of 0.15 mm thick is formed in the same manner as mentioned above from a mixture of 90 parts by weight of Al_2O_3 and 10 parts by weight of an oxide binder of Al_2O_3 (30 wt. %) - SiO_2 (53 wt. %) - MgO (17 wt. %). The green sheet is cut with the same size as the first and second solid electrolyte plates 3 and 4 to give an insulating layer 8b, which is drilled to have a gas introducing hole 9a. On the jointing surface 11b of the insulating layer 8b, a heater 1A is formed by using a platinum paste obtained by mixing a platinum powder with an organic material and by using a screen printing method. An insulating layer 8a having a gas introducing hole 9a is formed in the same manner with the same size as in the case of the insulating layer 8b (but having no heater on the joining surface 11).

A green sheet of 0.25 mm thick is prepared in the same manner as mentioned above from a mixture of ZrO_2 powder partially stabilized with 6 mole % Y_2O_3

containing 3% by weight of Al_2O_3. The green sheet is cut in the same size as the green sheet of solid electrolyte plate 3 and a gas introducing hole 9b (the same place as the gas introducing holes 9a of the insulating layers 8a and 8b) is drilled to give an intermediate layer 12.

The five thus prepared green sheets are laminated so that the green sheets of the solid electrolyte plates 3 and 4 and the porous electrodes 5, 6 and 7 are placed alternately, and the green sheet of intermediate layer 12 is laminated on the porous electrode 7 so as to form the gas chamber 10 over the electrode 7, followed by lamination of the green sheets of insulating layers 8b and 8a in this order so as to face the joining surfaces 11b and 11a and to connect the gas introducing holes 9a and 9b.

The laminated product is hot pressed at 120°C under a pressure of 80 kgf/cm^2, followed by sintering at 1500°C for 2 hours in the air. The organic material layer 13 is burnt at about 300°C during the sintering. Then, magnesium spinel is flame sprayed on the porous electrode 5 exposed to the outside to form a protective layer 14. Thus, the objected oxygen sensor element 2A is produced.

According to above-mentioned embodiment, since the first and second solid electrolyte plates 3 and 4 are laminated, and a pair of insulating layers 8a and 8b forming the heater 1A at the joining surface 11b are

laminated thereon via the intermediate layer 12, followed by sintering, there are many advantages in that it is not necessary to attach the heater 1 from the outside as the prior art indirectly heating and solid electrolyte type oxygen sensor shown in Fig. 10, the production of solid electrolyte type oxygen sensors becomes easy, and there is no fear of breaking the wire of the heater 1 during the production process.

In the above-mentioned embodiment, the organic material layer 13 is formed on the porous electrode 7 on the green sheet of the second solid electrolyte plate 4. But the formation of the organic material layer 13 as the core is not always necessary. But the formation of the organic material layer 13 can completely prevent the deformation of the gas chamber 10 caused by the lamination of the intermediate layer 12, so that there is an advantage in that there can be obtained the largest effective area of the porous electrode 7 with which the gas to be measured flowed to the gas chamber 10 contacts during the operation of the oxygen sensor.

As mentioned above, according to this invention, there can easily be produced oxygen sensor elements having a built-in heater, which oxygen sensor elements save remarkably the consuming electric power for heating the heater and it becomes possible to control the temperature of the oxygen sensor element with high precision.

CLAIMS

1. A solid electrolyte type oxygen sensor element having a built-in heater comprising porous electrodes and solid electrolyte plates containing ZrO_2 as a major component placed alternately, an insulating layer formed on an electrode formed side of one of the solid electrolyte plates so as to have a gas introducing hole and a gas chamber connected thereto and formed over the electrode, said insulating layer including a heater and containing Al_2O_3 as a major component, an oxide binder solid soluble in both the solid electrolyte and the insulating layer being added either to one of the solid electrolyte plate and the insulating layer, or to an insulating thin layer containing Al_2O_3 as a major component and formed at an interface of the solid electrolyte plate and the insulating layer.

2. A solid electrolyte type oxygen sensor element according to Claim 1, wherein the oxide binder is a metal oxide of Al_2O_3 - SiO_2 - MgO system having compositions in the region encircled by curves A - B - C - D - E - A in the triangular diagram of Fig. 9 and the points A to E having the following compositions in percents by weight:

	Al_2O_3	SiO_2	MgO
A	14.5	82.0	3.5
B	5.0	65.0	30.0
C	8.3	58.7	33.0
D	22.7	46.5	30.8
E	37.6	45.6	16.8

3. A solid electrolyte type oxygen sensor element according to Claim 1, wherein the oxide binder is a metal oxide of Al_2O_3 - SiO_2 system containing Al_2O_3 in an amount of 5 to 30% by weight and SiO_2 in an amount of 70 to 95% by weight.

4. A solid electrolyte type oxygen sensor element according to Claim 1, wherein the oxide binder is contained in either the insulating layer or the solid electrolyte plate or the insulating thin layer in an amount of 5 to 15% by weight.

5. A solid electrolyte type oxygen sensor element according to Claim 1, which further comprises an intermediate layer between the insulating layer and the solid electrolyte plate, said intermediate layer being made of a metal oxide mixture which reacts with the insulating layer and the solid electrolyte plate at the time of sintering and has a linear thermal expansion coefficient value between that of the solid electrolyte plate and that of insulating layer.

6. A solid electrolyte type oxygen sensor element according to Claim 5, wherein the metal oxide mixture

is partially stabilized ZrO_2 and 1.5 to 4% by weight of Al_2O_3.

7. A solid electrolyte type oxygen sensor element according to Claim 5, which further comprises a protective layer formed on an electrode exposed to an outside atmosphere.

8. A process for producing a solid electrolyte type oxygen sensor element having a built-in heater of Claim 1, which comprises

constructing a green sheet laminate by forming electrodes on green sheets of solid electrolyte plates containing ZrO_2 as a major component wherein the electrodes and solid electrolyte plates placed alternately,

placing a green sheet of insulating layer including a heater therein, containing Al_2O_3 as a major component and having a gas introducing hole on an electrode formed side of solid electrolyte plate so as to form a gas chamber over the electrode,

forming an insulating thin layer containing Al_2O_3 as a major component and an oxide binder solid soluble in both the solid electrolyte and the insulating layer at an interface of the insulating layer and the solid electrolyte plate provided that the oxide binder is not previously added to either the solid electrolyte plate or the insulating layer,

pressing the green solid electrolyte plates and the green insulating layer and the insulating thin layer

if contained, and

sintering the resulting pressed product.

9. A process for producing a solid electrolyte type oxygen sensor element having a built-in heater of Claim 5, which comprises

constructing a green sheet laminate by placing porous electrodes and solid electrolyte plates alternately, said solid electrolyte plates containing ZrO_2 as a major component and forming the electrode thereon,

placing a green sheet of intermediate layer made of a metal oxide mixture which reacts with the solid electrolyte plate and an insulating layer at the time of sintering and has a thermal expansion coefficient value between that of the solid electrolyte plate and that of the insulating layer, on an electrode formed side of solid electrolyte plate so as to form a gas chamber over the electrode,

placing a green sheet of insulating layer including a heater therein, containing Al_2O_3 as a major component and having a gas introducing hole on the intermediate layer,

pressing the green solid electrolyte plates, the green intermediate layer, and the green insulating layer, and

sintering the resulting pressed product.

10. A process according to Claim 9, which further comprises ceramic spraying magnesium spinel on the

electrode exposed to an outside atmosphere to form a protective film thereon.

FIG. 1

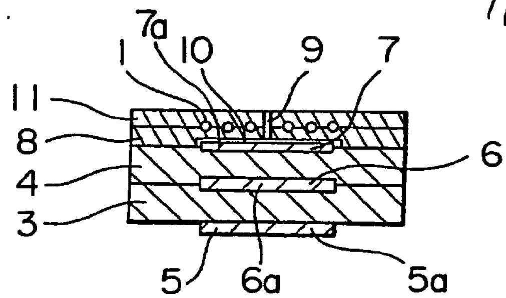

FIG. 2

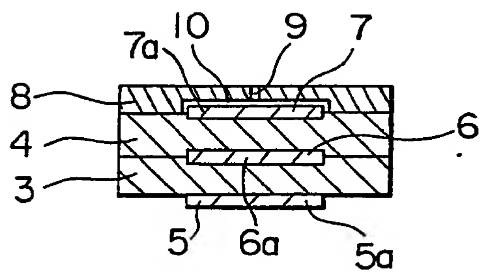

FIG. 3

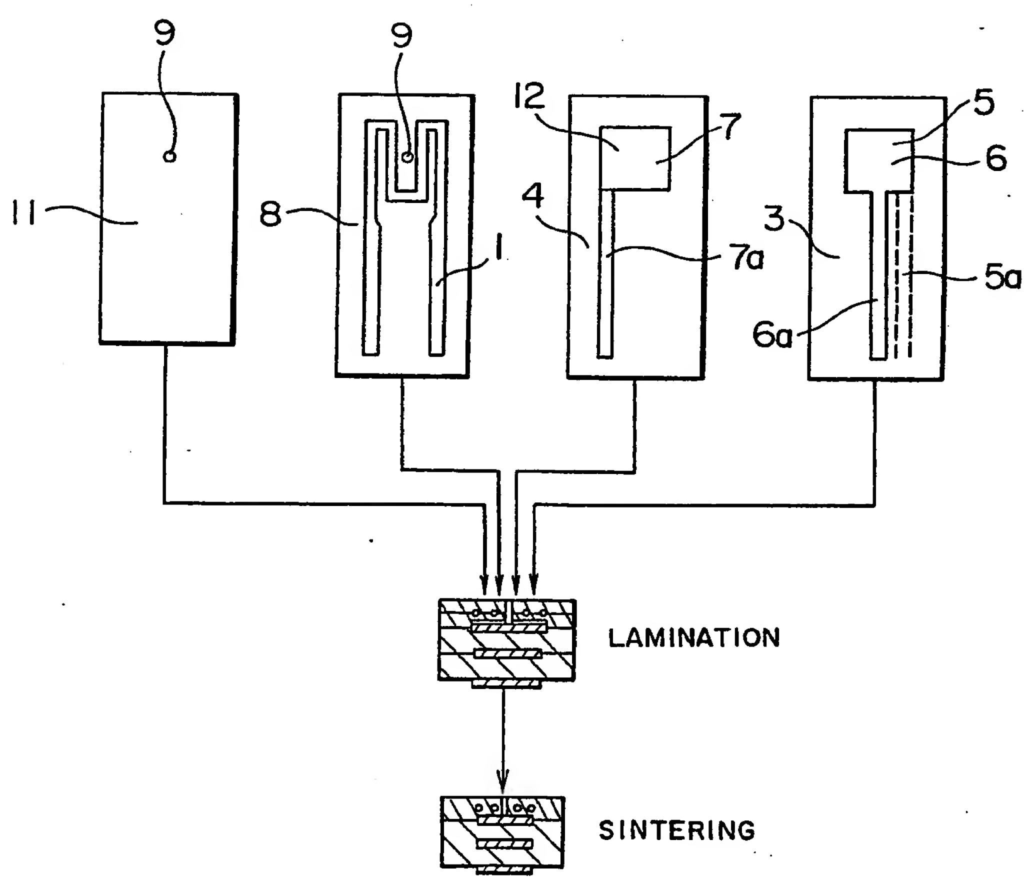

FIG. 4

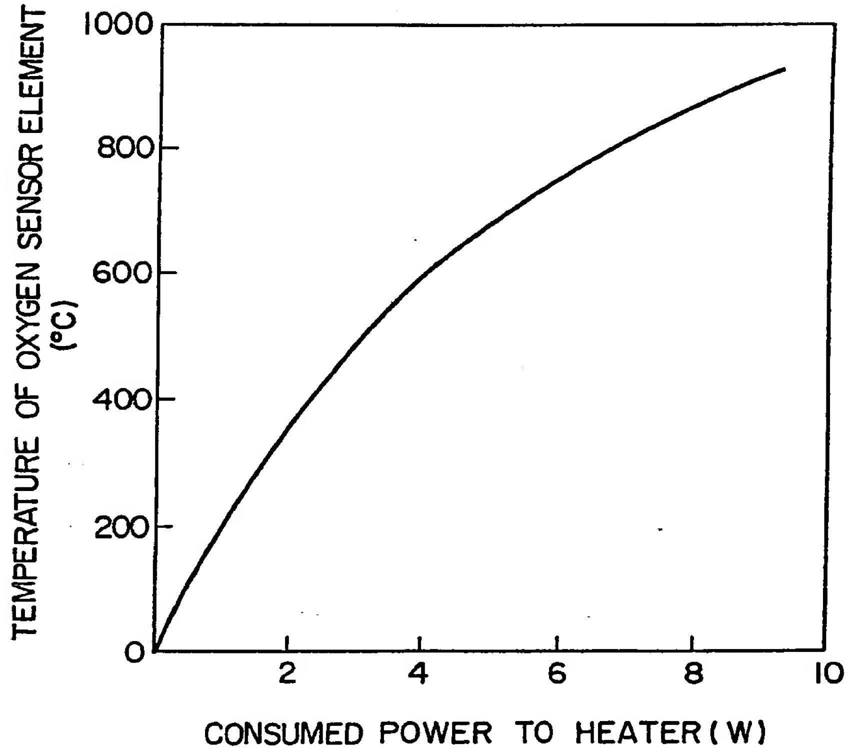
TEMPERATURE OF OXYGEN SENSOR ELEMENT (°C)
1000
800
600
400
200
0
2
4
6
8
10
CONSUMED POWER TO HEATER (W)

FIG. 5

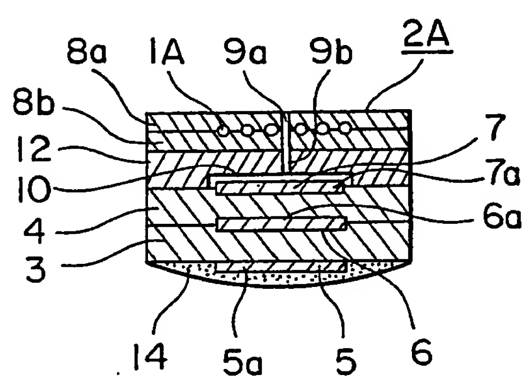
2A
8a
1A
9a
9b
8b
12
10
4
3
7
7a
6a
14
5a
5
6

FIG. 6

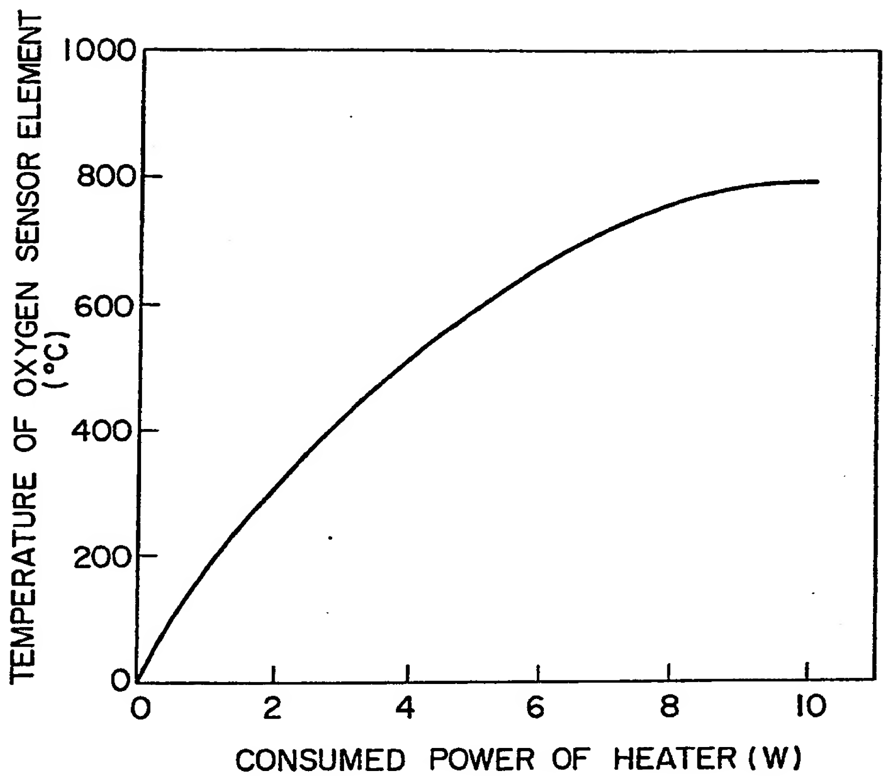
TEMPERATURE OF OXYGEN SENSOR ELEMENT (°C)
1000
800
600
400
200
0
0
2
4
6
8
10
CONSUMED POWER OF HEATER (W)

FIG. 7

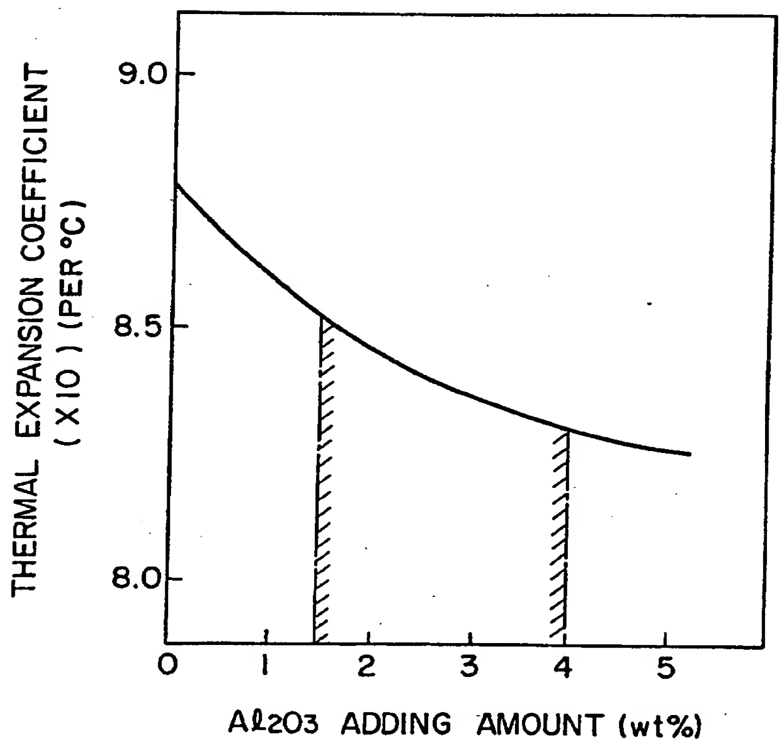
THERMAL EXPANSION COEFFICIENT
(X10) (PER °C)
9.0
8.5
8.0
0
1
2
3
4
5
Al2O3 ADDING AMOUNT (wt%)

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FIG. 8

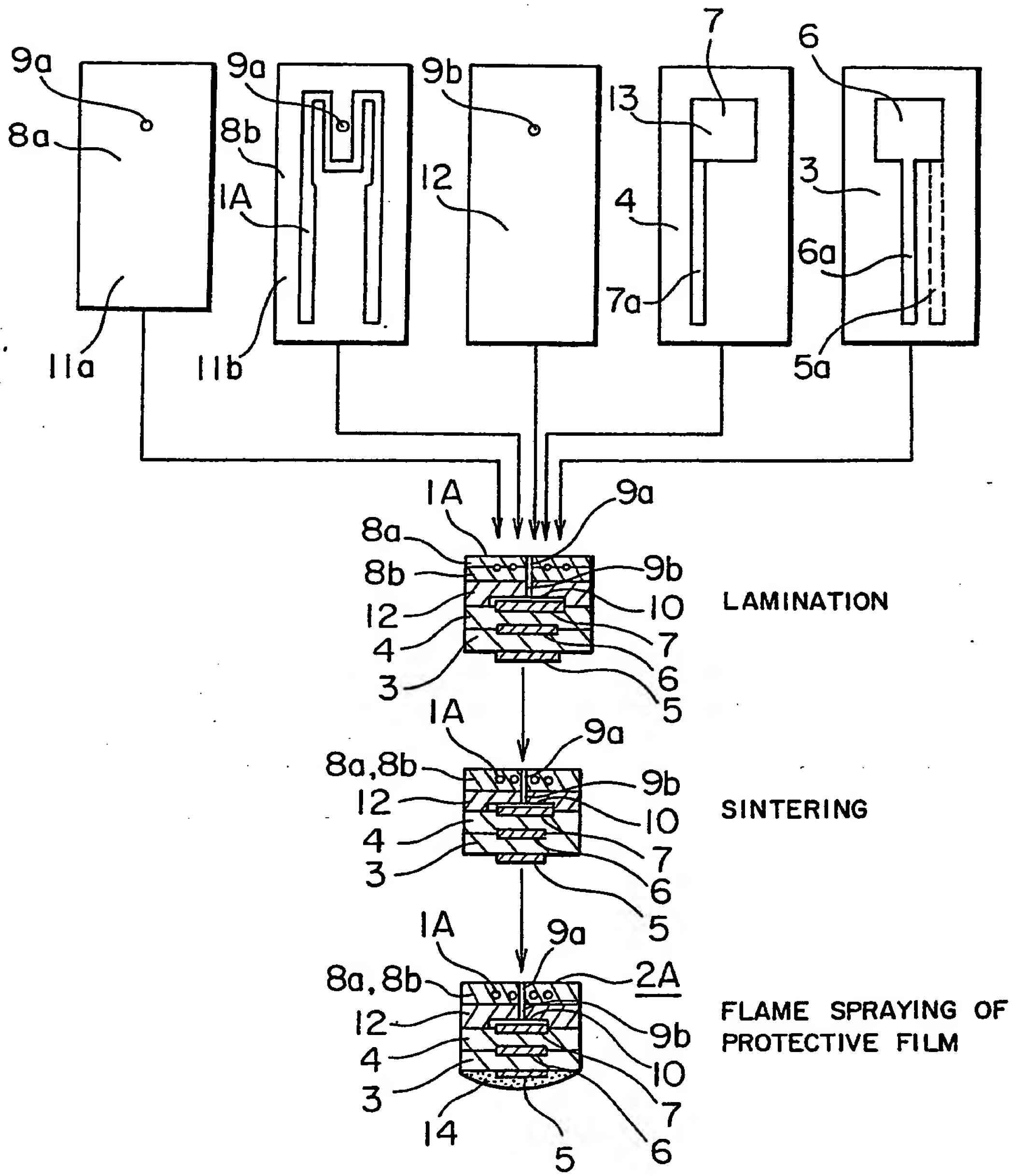

9a
8a
11a
9a
8b
1A
11b
9b
12
13
7
4
7a
6
3
6a
5a
1A
9a
8a
8b
12
4
3
9b
10
7
6
5
LAMINATION
1A
9a
8a,8b
12
4
3
9b
10
7
6
5
SINTERING
1A
9a
8a,8b
12
4
3
14
2A
9b
10
7
6
5
FLAME SPRAYING OF
PROTECTIVE FILM

FIG. 9

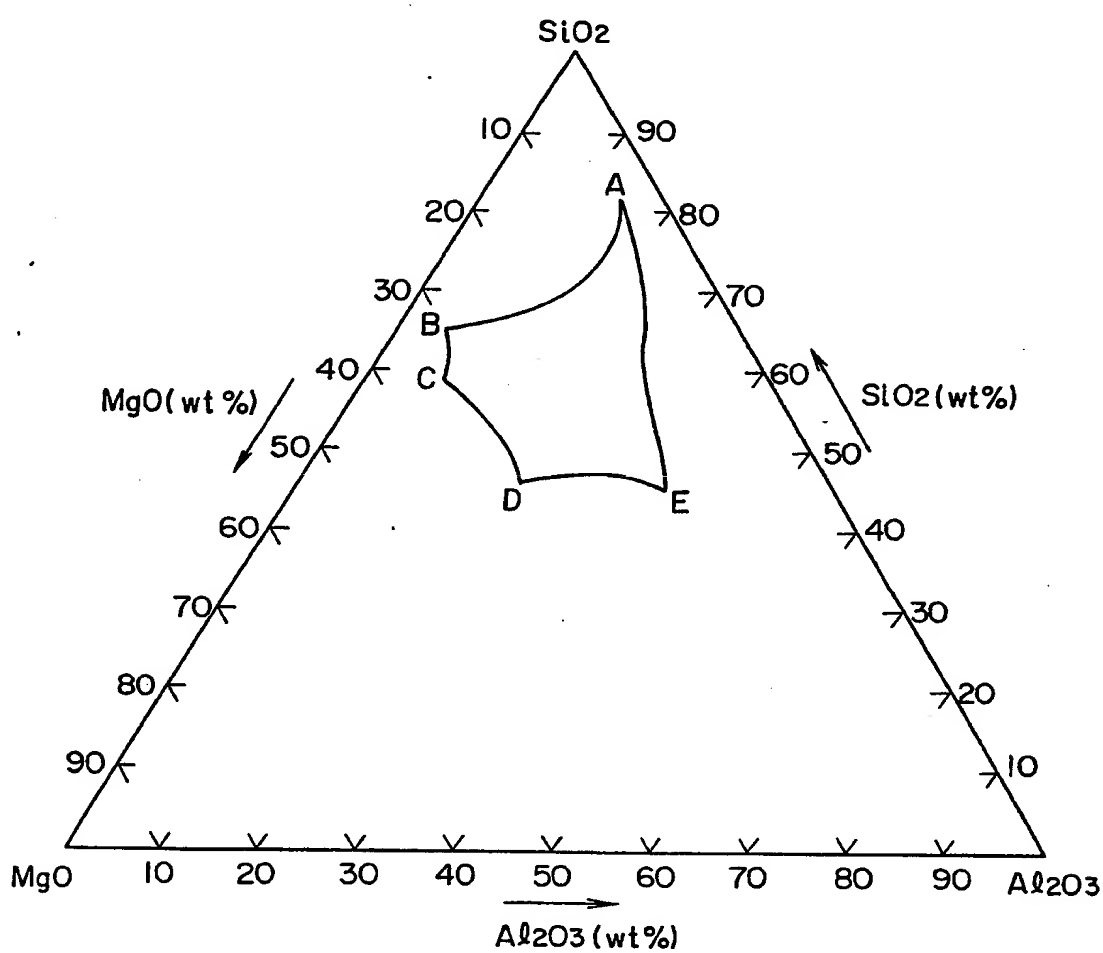

SiO2
10
20
30
40
50
60
70
80
90
90
80
70
60
50
40
30
20
10
A
B
C
D
E
MgO(wt %)
SiO2(wt%)
MgO
Al2O3
Al2O3(wt%)

FIG. 10

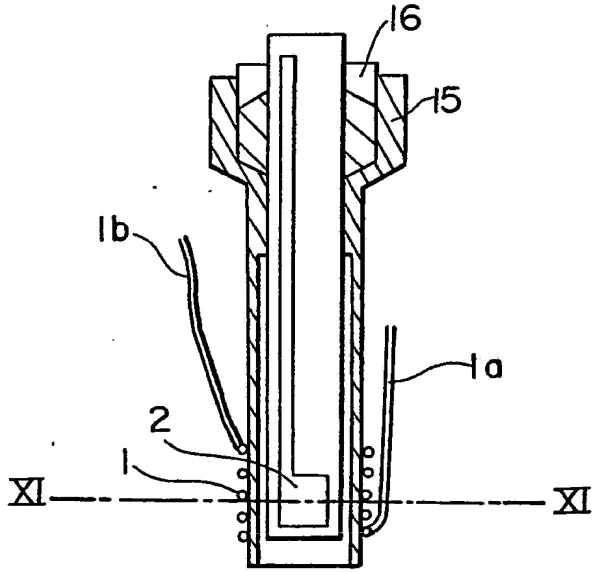
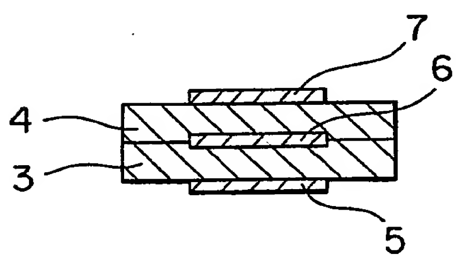


FIG. 11



European Patent Office

EUROPEAN SEARCH REPORT

0203351

Application number

EP 86 10 5424

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	EP-A-0 133 820 (NGK INSULATORS, LTD.) * whole document *	1	G 01 N 27/56
A	EP-A-0 134 709 (NGK INSULATORS, LTD.) * whole document *	1	
A	DE-A-2 907 032 (R. BOSCH GMBH) * whole document *	1	
A,P	EP-A-0 162 603 (NGK INSULATORS, LTD.) * whole document *	1,8,9	
A,P	EP-A-0 148 622 (NGK INSULATORS, LTD.) * whole document *	1,8,9	TECHNICAL FIELDS SEARCHED (Int. Cl.4) G 01 N 27/56
A	US-A-4 507 191 (NGK SPARK PLUG CO., LTD.) * whole document *	1,8,9	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	31-07-1986	BRISON O.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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